

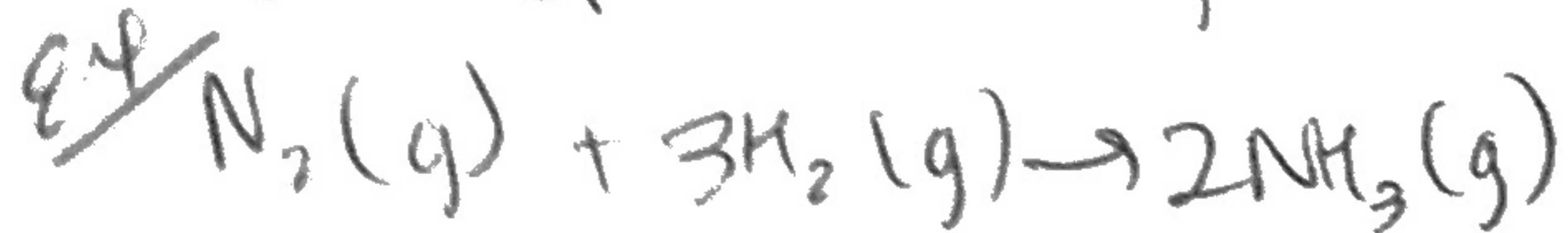
Kinetics & Rate Laws

Intro to Rate Laws

- rate law: means by which we can relate the rate of a chem rxn to [reactants]
- the rate law for a rxn is dep. on the specifics of how a rxn proceeds called the mechanism
 - what bonds 'break first', form first, any intermediate chem species
- determ. rate law for a rxn \rightarrow gain insight into potential mechanisms
 - \rightarrow connect macroscopic w/ microscopic/mic ideas
- chem. kinetics: study of rates of chem. change
- look @ C & T to see what aff. rxn to explain how bonds broken/made
- helps max. rate from products once you know mech. + what to manipulate

Reaction Rates

- rate of a chem. rxn is a measure of how fast the rxn is proceeding.
 - measure of Δ in C of chem. species as a fun of time
- C_{react} + C_{prod} relat. by balanced chem. eq. \rightarrow relate Δ to the coefficients



- rate consumption of N_2 gas is related to the rate of form. of NH_3 gas
- for each mole N_2 consumed, 2 moles NH_3 formed \rightarrow rate form NH_3 will be 2x rate loss N_2

$$-\frac{\Delta[N_2]}{\Delta t} = \frac{+\Delta[NH_3]}{2\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \text{rate}$$

- $\Delta[N_2]$ for some period time = $\Delta[NH_3]$ for the same period time $\div 2$ (b/c happens 2x as fast)

$$-\frac{d[N_2]}{dt} = \frac{+d[NH_3]}{2dt} = \frac{-d[H_2]}{3dt} = \text{rate}$$

• take deriv w/c above = for finite period of time

- doesn't really work when there are intermediate steps and products

Factors Affecting Rates

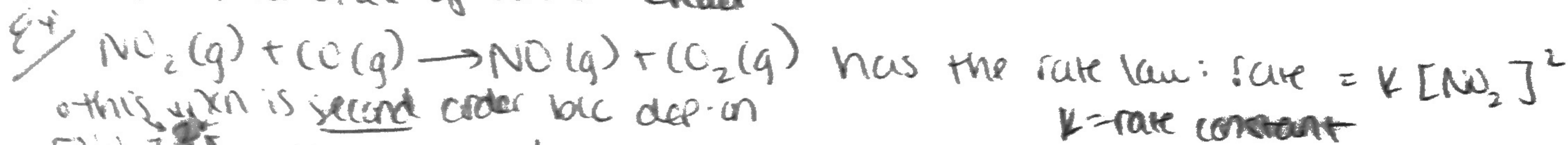
4 categories

- ① medium: physical state of the reactants since rate dep. on details of ^{the} rxn mech.
 - Ex/ outside rxn vss more quickly than inside b/c more exposed to O_2
- ② concentration: way C aff. rate tells us a lot about how rxn is happening (mech.)
 - relat. law rate + C = rate law: measured experimentally since can't be determ. by looking @ a balanced eq.
- ③ temperature: important b/c typically there is an ϵ barrier btw react. + prod.
 - means you make any new bonds of products, need to break bonds in react. or form some intermediate compd. that are usually higher in ϵ
 - only mols w/ sufficient ϵ will react \rightarrow @ higher T, more mols will have sufficient ϵ
 - \rightarrow nearly all rxns have faster rate @ higher T
- ④ catalyst: catalyst is a compd. that Δ reaction mech \rightarrow allow to proceed @ a faster rate
 - is part of the rxn mech but is not consumed during the chem rxn and doesn't appear as a react. nor prod.
 - role = lower ϵ barrier btw react. + prod. allowing rxn to proceed @ faster rates @ lower T

Empirical Rate Laws

Rate laws for an overall chem rxn cannot be deduced from the written rxn but must be determ. from experiments (this is the name "empirical")

• rate law relates rate of rxn to C_{react}



• this rxn is second order b/c dep. on $[NO_2]^2$

• is zeroth order in CO since dep. on $[CO]^0$ aka doesn't dep. on $[CO]$

• overall order = 2 = sum of all orders of the reactants (2+0=2)

• rate laws will always have the same form: $rate = k (C_{react})^{\text{power}}$ units: $M s^{-1}$

• usually only 0th-2nd order

↳ rate constant will have whatever units necessary to make $M s^{-1}$

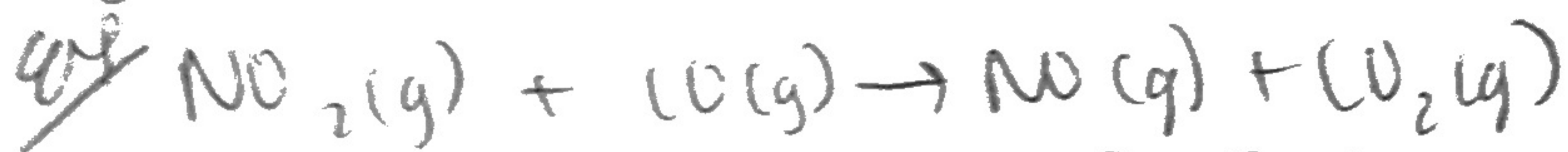
Ex: 1st order: $rate = k C_{react}$ so $k = s^{-1}$

2nd order: $rate = k (C_{react})^2$ so then $k = M^{-1} s^{-1}$

Determining Rate Laws

• run series of experiments w/ diff initial conditions + compare the very initial rate of rxn to avoid measuring backward rxns + since rate ↓ as time

• by $\Delta C_{initial}$ we can see what C_{off} rate + in what way



Experiment	initial $[NO_2] (M)$	initial $[CO] (M)$	initial rate ($M s^{-1}$)
1	5×10^{-4}	1.6×10^{-2}	2.8×10^{-9}
2	5×10^{-4}	3.2×10^{-2}	2.8×10^{-9}
3	1.5×10^{-3}	3.2×10^{-2}	2.5×10^{-8}

rate Δ 's when $[NO_2] \Delta$

$[NO_2]$ inc x3

+ rate inc x9

→ know is $[NO_2]^2$ b/c $9=3^2$

now know $rate = k [NO_2]^2$

Solve for k $k = \frac{2.8 \times 10^{-9}}{(5.0 \times 10^{-4})^2} = 0.011 M^{-1} s^{-1}$

• is 2nd order → must involve some bimolecular step that involves collision b/w

2 NO_2 molecules based on second order NO_2

• care about rate laws b/c give us insight into mech of rxns